

## PATENT ABSTRACTS OF JAPAN

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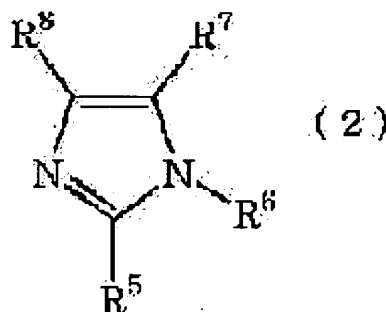
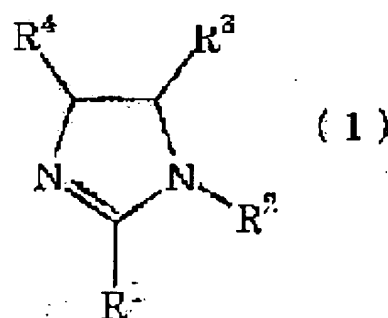
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## (54) METHOD FOR PRODUCING CYCLIC AMIDINIUM ORGANIC ACID SALT

## (57)Abstract:

PROBLEM TO BE SOLVED: To provide a simplified method for producing a cyclic amidinium organic acid salt having high purity.

SOLUTION: The cyclic amidinium organic acid salt is produced by reacting an organic acid with a cyclic amidine expressed by formula

(1) (R<sup>1</sup>, R<sup>3</sup> and R<sup>4</sup> are each independently H, an aliphatic group, an aromatic group or an aroaliphatic group; and R<sup>2</sup> is an aliphatic group, an aromatic group or an aroaliphatic group) or formula (2)(R<sup>5</sup>, R<sup>7</sup> and R<sup>8</sup> are each independently H, an aliphatic group, an aromatic group or an aroaliphatic group; and R<sup>6</sup> is independently an aliphatic group, an aromatic group or an aroaliphatic group).

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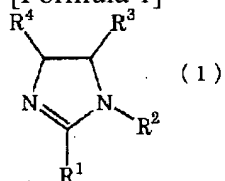
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## CLAIMS

[Claim(s)]

[Claim 1] The following general formula (1)

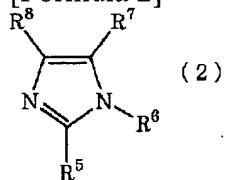
[Formula 1]



(R1, R3, and R4 express respectively independently the radical of a hydrogen atom or aliphatic series, aromatic series, or aroma aliphatic series among a formula, and R2 expresses the radical of aliphatic series, aromatic series, or aroma aliphatic series.)

Or the following general formula (2)

[Formula 2]



(In R5, R7, and R8, R6 expresses respectively independently the radical of aliphatic series, aromatic series, or aroma aliphatic series independently for the radical of a hydrogen atom or aliphatic series, aromatic series, or aroma aliphatic series among a formula.) The manufacture approach of the annular friend JINIUMU organic-acid salt characterized by making organic-acid ester react to the annular amidine expressed.

[Claim 2] In a general formula (1) a substituent R1, a substituent R3, and a substituent R4 The phenyl group permuted respectively independently by a hydrogen atom, the alkyl group of carbon numbers 1-4, the phenyl group, the alkyl group of carbon numbers 1-4, or the alkoxy group is expressed. The manufacture approach of an annular friend JINIUMU organic-acid salt according to claim 1 that a substituent R2 is characterized by expressing the phenyl group permuted by the alkyl group of carbon numbers 1-4, the phenyl group, the alkyl group of carbon numbers 1-4, or the alkoxy group.

[Claim 3] In a general formula (2) a substituent R5, a substituent R7, and a substituent R8 The radical of the aromatic series permuted respectively independently by a hydrogen atom, the alkyl group of carbon numbers 1-4, the phenyl group, the alkyl group of carbon numbers 1-4, or the alkoxy group is expressed. The manufacture approach of an annular friend JINIUMU organic-acid salt according to claim 1 that a substituent R6 is characterized by expressing the phenyl group permuted by the alkyl group of carbon numbers 1-4, the phenyl group, the alkyl group of carbon numbers 1-4, or the alkoxy group.

[Claim 4] The manufacture approach of the annular friend JINIUMU organic-acid salt according to claim 1 to 3 characterized by containing the alkyl group chosen from the group which organic-acid ester becomes from a methyl group, an ethyl group, n-propyl group, and n-butyl.

[Claim 5] The manufacture approach according to claim 1 to 3 that organic-acid ester is characterized by being a dimethyl phthalate, methyl benzoate, a methyl salicylate, methansulfonic acid methyl, p-toluenesulfonic-acid methyl, a diethyl phthalate, ethyl benzoate, ethyl salicylate, or p-toluenesulfonic-acid ethyl.

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## DETAILED DESCRIPTION

## [Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the manufacture approach of an annular friend JINIUMU organic-acid salt. An annular friend JINIUMU organic-acid salt can be used as the electrolytic solution by selecting a specific anion kind.

[0002]

[Description of the Prior Art] Conventionally, the method of making alkyl halide react to the nitrogen atom in an amidine as the manufacture approach of an annular friend JINIUMU salt is learned for many years. Moreover, the attempt using the carbonic acid diester which does not contain a real halogen is also performed.

[0003]

[Problem(s) to be Solved by the Invention] However, in order to obtain an annular friend JINIUMU organic-acid salt, once alkylating an annular amidine, anion exchange needed to be carried out at the desired organic acid. Therefore, the process was complicated by needing an anion exchange process. Moreover, the anion exchange to an organic-acid salt from a halogen is difficult.

[0004] This invention is made in view of the above-mentioned technical problem, and the purpose is offering the approach the annular friend JINIUMU organic-acid salt of a high grade being manufactured in the process by which simple was carried out.

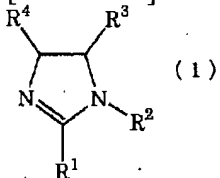
[0005]

[Means for Solving the Problem] this invention persons came to complete this invention, as a result of examining wholeheartedly the manufacture approach of obtaining an annular friend JINIUMU organic-acid salt by high yield easily.

[0006] That is, this invention is the following general formula (1).

[0007]

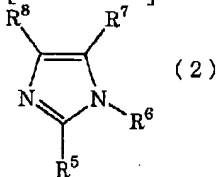
[Formula 3]



(In R<sup>1</sup>, R<sup>3</sup>, and R<sup>4</sup>, R<sup>2</sup> expresses respectively independently the radical of aliphatic series, aromatic series, or aroma aliphatic series for the radical of a hydrogen atom or aliphatic series, aromatic series, or aroma aliphatic series among a formula.) Or the following general formula (2)

[0008]

[Formula 4]



(-- in R<sup>5</sup>, R<sup>7</sup>, and R<sup>8</sup>, R<sup>6</sup> expresses respectively independently the radical of aliphatic series, aromatic series, or

aroma aliphatic series independently for the radical of a hydrogen atom or aliphatic series, aromatic series, or aroma aliphatic series among a formula.) -- it is the manufacture approach of the annular friend JINIUMU organic-acid salt characterized by making organic-acid ester react to the annular amidine expressed.

[0009] Hereafter, this invention is explained to a detail.

[0010] The annular amidine used in the approach of this invention is a compound shown by the above-mentioned general formula (1) or the above-mentioned general formula (2).

[0011] In the annular amidine shown by the above-mentioned general formula (1) as a substituent R1, a substituent R3, and a substituent R4 The phenyl group permuted respectively independently by a hydrogen atom, the alkyl group of carbon numbers 1-4, the phenyl group, the alkyl group of carbon numbers 1-4, or the alkoxy group is desirable. As a substituent R2 The phenyl group permuted by the alkyl group of carbon numbers 1-4, the phenyl group, the alkyl group of carbon numbers 1-4, or the alkoxy group is desirable. In the annular amidine shown by the above-mentioned general formula (2) moreover, as a substituent R5, a substituent R7, and a substituent R8 The radical of the aromatic series permuted respectively independently by a hydrogen atom, the alkyl group of carbon numbers 1-4, the phenyl group, the alkyl group of carbon numbers 1-4, or the alkoxy group is desirable. The phenyl group permuted as a substituent R6 by the alkyl group of carbon numbers 1-4, the phenyl group, the alkyl group of carbon numbers 1-4, or the alkoxy group is desirable.

[0012] As an annular amidine shown by the above-mentioned general formula (1) Although it does not limit especially, specifically 1-methyl imidazoline, 1, 2-dimethyl imidazoline, 1, 4-dimethyl imidazoline, 1, 5-dimethyl imidazoline, 1, 2, 4-trimethyl imidazoline, 1 and 2, 6-trimethyl imidazoline, The methyl group in 1, 2, 4, 6-tetramethyl imidazoline, and these imidazoline compound What was permuted by an ethyl group, n-propyl group, i-propyl group, n-butyl, n-pentyl radical, n-hexyl group, the phenyl group, etc. is mentioned. Preferably among these They are 1-methyl imidazoline, 1, 2-dimethyl imidazoline, 1-ethyl IMIDARIN, and 1-ethyl-2-methyl imidazoline.

[0013] Moreover, the annular amidine shown by the above-mentioned general formula (2) and the bottom Although it does not limit especially, specifically 1-methyl imidazole, 1, 2-dimethyl imidazole, 1, 4-dimethyl imidazole, 1, 5-dimethyl imidazole, 1, 2, a 4-trimethyl imidazole, 1 and 2, a 6-trimethyl imidazole, 1, 2, 4, a 6-tetramethyl imidazole, and the methyl group in these imidazoles compound What was permuted by an ethyl group, n-propyl group, i-propyl group, n-butyl, n-pentyl radical, n-hexyl group, the phenyl group, etc. is mentioned. Preferably among these They are 1-methyl imidazole, 1, 2-dimethyl imidazole, 1-ethyl imidazole, and 1-ethyl-2-methylimidazole.

[0014] The annular amidine shown by the above-mentioned general formula (1) is compoundable by the well-known approach. For example, 1-ethyl-2-methyl imidazoline can be easily obtained by making it react with an acetonitrile and N-ethyl ethylenediamine under existence of a metal salt or an acid catalyst.

[0015] In the approach of this invention, an annular amidine and the organic-acid ester made to react contain a methyl group, an ethyl group, n-propyl group, or n-butyl preferably. Such organic-acid ester can be easily obtained by the reaction of organic acids, such as a formic acid, an acetic acid, a propionic acid, oxalic acid, a malonic acid, a maleic acid, a succinic acid, a fumaric acid, an acrylic acid, methacrylic acid, a phthalic acid, a benzoic acid, a salicylic acid, methansulfonic acid, and p-toluenesulfonic acid, and alcohol, such as a methanol, ethanol, n-propanol, and n-butanol.

[0016] As organic-acid ester used in the approach of this invention, methyl formate, methyl acetate, methyl propionate, oxalic acid dimethyl, dimethyl malonate, maleic-acid dimethyl, succinic-acid dimethyl, dimethyl fumarate, a methyl acrylate, methacrylic acid methyl, a dimethyl phthalate, methyl benzoate, a methyl salicylate, methansulfonic acid methyl, p-toluenesulfonic-acid methyl, etc. are illustrated, and, specifically, the organic-acid ester which transposed this methyl group to an ethyl group, n-propyl group, or n-butyl further is also mentioned. The dimethyl phthalate from a reactant viewpoint, methyl benzoate, a methyl salicylate, methansulfonic acid methyl, p-toluenesulfonic-acid methyl, a diethyl phthalate, ethyl benzoate, ethyl salicylate, and p-toluenesulfonic-acid ethyl are [ among these ] desirable. Generally these organic-acid ester is marketed and can come to hand easily.

[0017] the amount of the organic-acid ester used in the approach of this invention -- an annular amidine -- receiving -- 1 - 2 double mol -- it is the range of an one to 1.3 time mol preferably.

[0018] In the approach of this invention, although especially reaction temperature is not limited, generally it is 100 degrees C - 140 degrees C, and there is a possibility that the annular friend JINIUMU organic-acid salt generated when the reaction was too slow, was not practical and exceeded 140 degrees C may decompose,

below 100 degrees C.

[0019] It is more desirable to use a solvent from the need of making it dissolving, when the annular amidine which is a raw material is a solid-state in the approach of this invention, although it is not necessary to use a solvent. If the annular amidine and organic-acid ester which are inactive and a raw material are dissolved in a reaction condition as a solvent, it can be especially used without a limit. However, since there is fear of hydrolysis when an annular amidine is an imidazoline compound, mixing of water must be avoided. As a solvent, for example Methyl alcohol, ethyl alcohol, n-propyl alcohol, i-propyl alcohol, n-butyl alcohol, i-butyl alcohol, sec-butyl alcohol, t-butyl alcohol, a cyclohexanol, Benzyl alcohol, ethylene glycol, propylene glycol, Alcohols, such as a diethylene glycol, triethylene glycol, and a glycerol, An acetonitrile, propionitrile, butyronitrile, valeronitrile, Ketones, such as nitril, such as a benzonitrile and acrylonitrile, an acetone, and a methyl ethyl ketone Sulfoxides, such as dimethyl sulfoxide, a sulfolane, and 3-methyl sulfolane A formamide, N-methyl formamide, N,N-dimethylformamide, Heterocycle type solvents, such as lactone, such as amides, such as an acetamide, N-methyl acetamide, N,N-dimethylacetamide, and N-methyl pyrrolidone, and other gamma-butyrolactone, and 1,3-dimethyl-2-imidazolidinone, etc. can be mentioned. Although especially the amount of the solvent used does not have a limit, it is desirable to make it 10 or less times by the weight ratio to an annular amidine. Even if it exceeds 10, the effectiveness which increased the solvent is small.

[0020] It is more desirable to carry out under pressurization, when using the solvent of a low-boiling point or the organic-acid ester of a low-boiling point although a reaction may be performed under ordinary pressure or you may carry out under pressurization in the approach of this invention.

[0021]

[Example] Hereafter, although an example explains the approach of this invention, this invention is not limited to these. In addition, high performance chromatography (TOSOH CORP. make) analyzed the purity analysis in an example.

[0022] After putting in and carrying out the nitrogen purge of 1-ethyl-2-methyl imidazoline 44.8g, methanol 40.0g, and the 77.7g of the dimethyl phthalates to the autoclave made from 1200ml stainless steel of examples, it heated at 135 degrees C and reacted for 8 hours. When this was cooled after reaction termination and the high speed liquid chromatography analyzed, the 1-ethyl-2-methyl imidazoline invert ratio was 90%, and the selectivity of 1-ethyl -2 and 3-dimethyl imidazolinium phthalic-acid methyl salt was 98%.

[0023] After putting in and carrying out the nitrogen purge of 1 and 2-dimethyl imidazole 38.5g, methanol 40.0g, and the 63.9g of the methyl salicylates to the autoclave made from 2200ml stainless steel of examples, it heated at 135 degrees C and reacted for 8 hours. When this was cooled after reaction termination and the high speed liquid chromatography analyzed, 1 and 2-dimethyl imidazole invert ratio was 91%, and the selectivity of 1, 2, and 3-trimethyl imidazolium salicylate was 99%.

[0024] After putting in and carrying out the nitrogen purge of 1 and 2-dimethyl imidazole 38.5g, methanol 40.0g, and the 69.8g of the ethyl salicylates to the autoclave made from 2200ml stainless steel of examples, it heated at 135 degrees C and reacted for 8 hours. When this was cooled after reaction termination and the high speed liquid chromatography analyzed, 1 and 2-dimethyl imidazole invert ratio was 78%, and the selectivity of 1-ethyl -2 and 3-dimethyl imidazolium salicylate was 99%.

[0025] After putting in and carrying out the nitrogen purge of 1 and 2-dimethyl imidazole 38.5g, acetonitrile 40.0g, and the 27.1g of the ethyl chlorides to the autoclave made from 1200ml stainless steel of examples of a comparison, it heated at 135 degrees C and reacted for 7 hours. When this was cooled after reaction termination and the high speed liquid chromatography analyzed, 1 and 2-dimethyl imidazole invert ratio was 90%, and the selectivity of 1-ethyl -2 and 3-dimethyl imidazolium was 97%. As a result of carrying out separation purification of the product, 57.0g 1-ethyl -2 and 3-dimethyl imidazolium chloride were obtained. The process of anion exchange was required separately to make this into an organic-acid salt, and it was difficult to carry out anion exchange of the chloride with an organic acid.

[0026] After putting in and carrying out the nitrogen purge of 1 and 2-dimethyl imidazole 38.5g, methanol 40.0g, and the 72.0g of the dimethyl carbonate to the autoclave made from 2200ml stainless steel of examples of a comparison, it heated at 135 degrees C and reacted for 7 hours. When this was cooled after reaction termination and the high speed liquid chromatography analyzed, 1 and 2-dimethyl imidazole invert ratio was 91%, and the selectivity of 1, 2, and 3-trimethyl imidazolium was 98%. As a result of carrying out separation purification of the product, the 63.3g 1, 2, and 3-trimethyl imidazolium methyl carbonate was obtained. The process of anion exchange was required separately to make this into an organic-acid salt.

[0027]

[Effect of the Invention] According to the approach of this invention, by selecting a specific anion kind, the annular friend JINIUMU organic-acid salt which can be used as the electrolytic solution can be easily manufactured by high yield, and the approach of this invention is very useful industrially.

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